

PATENT SPECIFICATION

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NO DRAWINGS

- (21) Application No. 10207/69 (22) Filed 26 Feb. 1969
(31) Convention Application No. 709 959 (32) Filed 4 March 1968 in
(33) United States of America (US)
(45) Complete Specification published 1 March 1972
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11P1C 11P1E5 11P1F 11P2C 11P2X 11P6A
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(72) Inventors FANNIE S. VARVERI, ROBERT J. JULA and M.
FREDERICK HOOVER



(54) RETENTION OF FILLERS AND FINES IN PAPER PRODUCTION

(71) We, CALGON CORPORATION, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Robinson Township, Allegheny County, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with retention aids in the paper industry.

In papermaking, retention is generally defined as the retaining of inorganic fillers, such as clay and titanium dioxide, as well as cellulosic fines within the paper sheet during manufacture (such as on a Fourdrinier machine). The retention obtained on the wire screen is a function of different mechanism such as filtration by mechanical entrainment, electrostatic attraction, and bridging between cellulosic fibers and filler. However, since both the cellulose and many common fillers are electronegative, they are mutually repellent and, in the absence of a retention aid the only factor tending to enhance retention is mechanical entrainment.

Generally, retention aids are used because of the high cost of pigments, such as titanium dioxide. The use of the retention aids adds considerably to the amount of such pigments incorporated into the wet web. In addition, the retention aid can appreciably reduce the suspended material in the paper-machine white-water effluent and so reduce the consequential pollution problem and loss of pigment.

Retention aids are commonly used in the manufacture of specialty paper finishes such as bond paper and "printing" paper, where high loadings of pigment and/or filler are required. The function of the retention aid is to bind the filler to the cellulosic fibers without mechanically blocking the pores in the paper sheet, thereby not adversely affecting the drainage properties of the wet paper web. This can be best

ERRATUM

SPECIFICATION No. 1,265,496

Page 1, Heading, (52) Index at acceptance,
after 8P1E5 insert 8P1F 8P2C 8P2X
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THE PATENT OFFICE
27th March 1972

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 (72) Inventors FANNIE S. VARVERI, ROBERT J. JULA and M.
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(54) RETENTION OF FILLERS AND FINES IN PAPER PRODUCTION

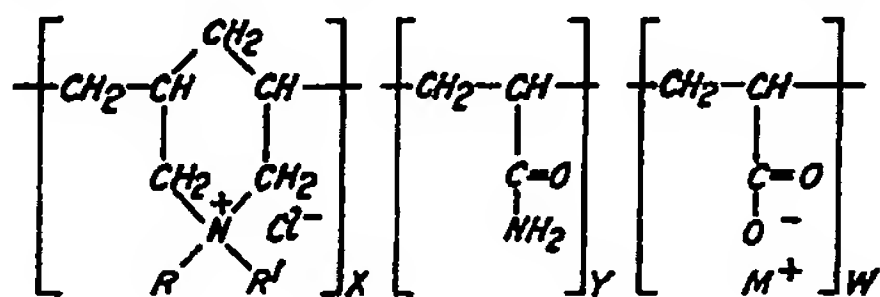
- (71) We, CALGON CORPORATION, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Robinson Township, Allegheny County, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —
- This invention is concerned with retention aids in the paper industry.
- In papermaking, retention is generally defined as the retaining of inorganic fillers, such as clay and titanium dioxide, as well as cellulosic fines within the paper sheet during manufacture (such as on a Fourdrinier machine). The retention obtained on the wire screen is a function of different mechanism such as filtration by mechanical entrainment, electrostatic attraction, and bridging between cellulosic fibers and filler. However, since both the cellulose and many common fillers are electronegative, they are mutually repellent and, in the absence of a retention aid the only factor tending to enhance retention is mechanical entrainment.
- Generally, retention aids are used because of the high cost of pigments, such as titanium dioxide. The use of the retention aids adds considerably to the amount of such pigments incorporated into the wet web. In addition, the retention aid can appreciably reduce the suspended material in the paper-machine white-water effluent and so reduce the consequential pollution problem and loss of pigment.
- Retention aids are commonly used in the manufacture of specialty paper finishes such as bond paper and "printing" paper, where high loadings of pigment and/or filler are required. The function of the retention aid is to bind the filler to the cellulosic fibers without mechanically blocking the pores in the paper sheet, thereby not adversely affecting the drainage properties of the wet paper web. This can be best accomplished by producing a microfloc of the filler, through the adsorption of the polymeric retention aid onto the cellulosic fibers which become charged and attract the oppositely charged pigment or filler.
- High-speed paper-making machines may run from 1,000 to 2,600 feet per minute, and some machines run at speeds of up to 3,500 feet per minute. Clearly, any adverse effect upon drainage characteristics will result in a reduction in the machine speed.
- Polyacrylamides in which about 3% to 35% of the amide groups have been hydrolysed to carboxylic acid groups have been used as retention aids in the past. Such a retention aid could adversely affect drainage properties as it may overfloc the pigment. It is essential for alum to be present for such a retention aid to work effectively, and the aid is effective only over a narrow pH range. The retention value can fluctuate as much as 20% with small variations of pH or alum loadings.
- U.S. Patents 2,884,058 and 3,077,430 disclose the use of certain acrylamide copolymers as dry-strength agents when used in certain concentrations.
- For high-quality paper filled with titanium dioxide, rosin is customarily used as

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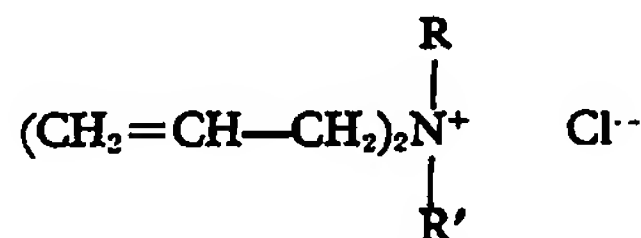
a size. Alum is used to set the rosin, i.e. to insolublize and fix the rosin, and also to make the paper system acidic. The alum may function as a link between the anionic pigment and the negatively charged cellulosic fiber, and also functions, to a degree, as a flocculant. Generally, the cellulosic pulp, on a dry basis, contains about 9.5% to 2% rosin, and has a minimum alum content of about 10—20 pounds per ton. However, paper mills customarily use about 40 pounds of alum per ton of dry pulp in order to ensure the desired pH range and rosin sizing. Also commonly used are synthetic sizes, such as that sold under the Trade Mark "Aquapel", which are cured at a neutral or alkaline pH; the anionic acrylamide polymers do not function effectively as retention aids in these systems.

The pH and alum load of paper systems are generally interdependent to a certain degree, although acids such as sulfuric acid may be added to the pulp to reduce the pH to a desired range in the case of low alum loads.

In accordance with the present invention, there is provided a method of improving the retention of inorganic filler and fine cellulosic material in the production of paper that comprises adding to an aqueous paper pulp suspension a linear amphionic copolymer of molecular weight at least 10000 having units of the general formulae:



in which each of R and R', which are similar or dissimilar, is a C₁₋₁₄ alkyl, β-propionamido or carboxymethyl radical and w, x and y are such that (w+y) : x lies within the range obtained by copolymerizing acrylamide and a diallyl quaternary ammonium chloride of formula:



in a weight ratio of from 3:7 to 7:3, x:w is from 100:1 to 2:1 and M⁺ is an alkali-metal or ammonium cation.

It is to be understood that the formulae throughout the specification and claims are intended to define the units and the proportions in which they appear and not to make any implication concerning their distribution in the linear chain.

The polymeric molecules used in the process of the present invention contain both positive and negative ionic charges and are of value as retention aids because their activity is less affected by variations in pH and the chemical content of the aqueous paper pulp suspension, so that the retention of cellulosic fines, fillers, pigments and other chemical additives is aided and improved and variations in alum load and pH have little or no adverse effect on the retention.

Diallyl-β-propionamidocarboxymethyl-ammonium chloride may be used as a monomer in the production of the polymers of the present invention. This monomer may be prepared by heating diallylamine at about 60° C for 5 hours with acrylamide to form diallyl-β-propionamidoamine and then treating this compound with the sodium salt of chloroacetic acid at 80° C for 8 hours, whereby a quaternary salt is formed with one positive site and one negative site. The diallyl-β-propionamidocarboxymethyl-ammonium chloride monomer may be considered as conferring amphionic properties upon the polymer, since it has both a positive charge and a negative charge site.

Among alkyl groups which may be represented by R and R', may be mentioned methyl, ethyl, propyl, isobutyl, hexyl, decyl, dodecyl, and octadecyl. Preferred substitutes are methyl and ethyl groups. Mixtures of various diallyl-ammonium chloride compounds of the above formula may be used as desired.

At the present time, economic considerations generally dictate the use of simply constituted monomeric materials, e.g. acrylamide itself, rather than chloroacrylamide, N, N-dimethyl-acrylamide, methacrylamide, or diacetone-acrylamide for instance, although these compounds may be used.

The weight ratio of the quaternary-ammonium chloride groups and the acrylamide groups can vary from 30/70 to 70/30 with preferred weight ratio being 50:50. At a 50:50 weight ratio of acrylamide: quaternary ammonium compound, in the case of dimethyl-diallyl-ammonium chloride, for example, the mole ratio of acrylamide to quaternary compound is about 2.27 to 1.0. Molecular weight of the polymer must be at least 10,000; so long as the polymer is water-soluble, higher molecular weights are preferred.

After polymerization, some of the acrylamide units are hydrolysed to carboxylic units. The polymer after hydrolysis may have from 100 to 2 and preferably 10 quaternary units per carboxylic unit. At the preferred ratio of 10 quaternary units per carboxylic group, about 4.3% of the amido groups will have been hydrolysed in a 50:50 dimethyl-diallyl-ammonium chloride: acrylamide copolymer.

In the hydrolysis reaction, it is preferred to use relatively dilute caustic alkali, for instance less than 20% concentration by weight in aqueous solution, with very good mixing at a temperature of about 60° C. The only effect the temperature variation will have is to modify the rate of hydrolysis. An alkali-metal or ammonium hydroxide or carbonate may be used in the hydrolysis reaction.

It is important that the diallyl-ammonium compound be a diallyl-ammonium chloride as only the chloride anion will allow the polymerization to proceed to the high-molecular-weight compounds usable in the present invention.

Particularly preferred retention-aid polymers are those obtained by polymerizing acrylamide with mixtures of dimethyl-diallyl-ammonium chloride and diethyl-diallyl-ammonium chloride. The ratio of the dimethyl-diallyl-ammonium chloride to the diethyl-diallyl-ammonium chloride may vary from 99:1 to 1:99, although the most suitable ratio is 95:5.

The formation of certain polymeric compounds from acrylamide and diallyl-quaternary-ammonium compounds is already known, as disclosed in, for instance, US Patents 2,923,701 and 3,147,218. In general, the polymers used in this invention may be made by similar techniques, the ratios of the monomers, the chloride anion and the hydrolysis step being as prescribed herein. Preferably, the reaction is conducted in an aqueous solution using a redox catalyst system, but any method capable of making the unhydrolysed copolymers desired herein is, of course, satisfactory, so long as the polymers have the required high molecular weight.

In practice, the catalyst may be added to the polymerization reactants over a period of time, and the temperature may be maintained at any convenient point where a set and controllable rate of polymerization is achieved. Such temperatures preferably lie in the range 20° to 90° C, preferably 30° to 75° C.

The concentration of alkali used to hydrolyse the cationic copolymer may be selected according to convenience, with the expected effects on the hydrolysis rate and the temperature required to achieve the desired hydrolysis in a convenient period of time. When this polymer structure is subjected to hydrolysis, the carboxamido groups are hydrolysed to carboxyl groups. In this manner, the ratio of cationic quaternary-ammonium to anionic carboxylic sites in the molecule may be varied and controlled, as desired, to achieve optimum properties.

The polymers of the present invention may be added to the paper pulp at any desired point effective to aid in the retention of fibers and additives in the paper as it is being formed on a paper machine. Generally, the retention aid will be added at a point prior to the forming surface. It is a particular feature of this invention that the introduction of the polymers described herein into the paper-making pulp will lead to an improved retention of the cellulosic fines and of the various additives especially pigment and fillers, over a wide range of pH and other chemical conditions. Further, there are observed improved retention characteristics as a result of the addition of these polymers over a wide range of alum-loading conditions. As is well known, the amount of alum used in the paper-making industry may vary widely, and it is desired to have a retention aid which will yield good retention characteristics over a wide range of alum concentrations. This desired characteristic has been demonstrated by the polymers of the present invention, as shown in connection with the working examples herein. The present invention provides amphionic polymeric retention aids which may vary no more than 10% in retention values across alum load ranges of 1 to 100 pounds of alum per ton of dry pulp, and across pH ranges of 3.5 to 8.0.

Generally, about 1/2 pound of retention aid per ton of dry pulp will be added to the paper pulp slurry. A retention aid will seldom be used in amounts of less than 0.1 pound per ton of dry pulp, and in normal practice the retention aid will

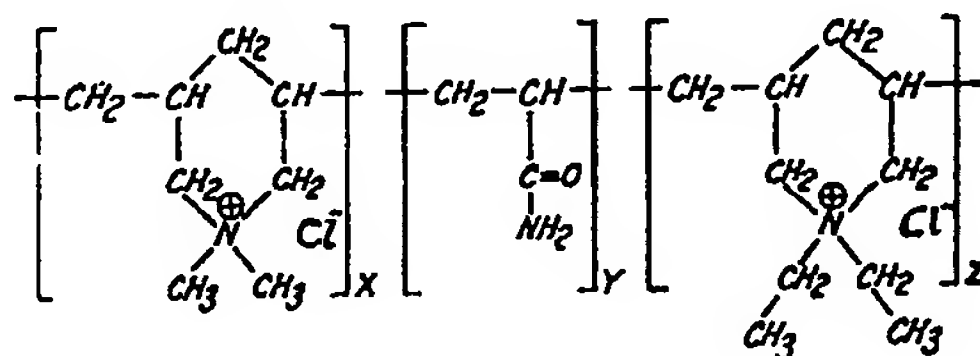
not be used in amounts higher than 2 pounds per ton of dry pulp for economic reasons, although in some cases more retention aid may be used without adverse effect, for instance, five or even 10 pounds per ton of dry pulp. Mixtures of retention aids may be used as desired. The retention aids of the present invention have essentially no detrimental effect on the dry strength of the paper when used in the above concentrations.

Generally, the polymers used in the method of the invention may be produced by the following procedure:

A monomer mixture comprising a 50/50 weight ratio of acrylamide to diallyl-quaternary-ammonium monomers at 20% total solids is prepared in aqueous solution. The pH of this monomer solution is adjusted to 6.5 with dilute NaOH solution and the solution is then heated to 50° C and held at this temperature while it is purged with nitrogen gas for a 1-hour period to remove all dissolved oxygen. To this monomer solution a redox polymerization catalyst system is added comprising an aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $\text{Na}_2\text{S}_2\text{O}_5$ in the following manner:

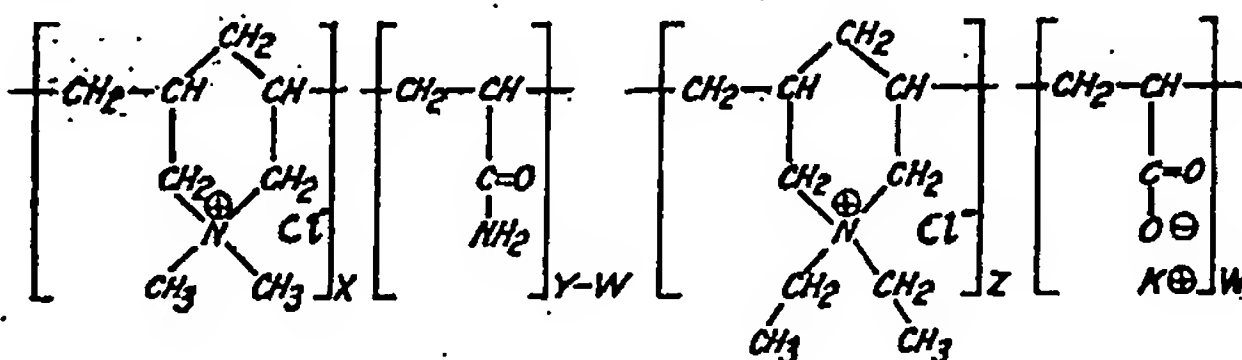
0.24% ammonium persulfate based on the weight of the monomer is added to the monomer mix. Then a dilute solution of sodium metabisulfite is pumped into the monomer solution at such a rate as to maintain a concentration of 6.58×10^{-7} moles of bisulfite per mole of total monomer. This bisulfite solution initiates and sustains the polymerization reaction at a controlled rate. The polymerization is normally conducted under adiabatic conditions so that the temperature of the solution rises from 50° C to about 75° C within about an hour.

The temperature is then held at about 60° C for an hour, producing a hyper-viscous aqueous solution of a water-soluble polymer, for example one having units of formulae:



in which $\frac{X+Z}{Y}$ is the figure resulting from polymerization of equal weights of acrylamide and the mixture of diallyl quaternary ammonium chlorides, X/Z is approximately 19, and the units are in a linear chain.

Again by way of illustration, the base polymer is then partially hydrolysed by treating the solution with an appropriate amount, for example the amount calculated to hydrolyse 4.3% of the amide groups, of a potassium hydroxide solution (20% solids) at a temperature of about 60° C for two hours. The resultant partially hydrolysed polymer has about 10 quaternary units to each carboxylic unit and is water-soluble. The units have the formulae



where $\frac{(X+Z)}{W}$ is about 10/1, and the units are in a linear chain.

The polymeric product may then be recovered as a dry flaked or powdered solid from the viscous solution by solvent precipitation using water-miscible organic solvents such as methanol or acetone, or by drum drying or other known techniques. Other substituted diallyl-ammonium monomers such as the β -propionamido monomers previously mentioned may be used with above generalized preparation.

The following Examples, in which 'Separan', 'Reten' and 'Mullen' are Trade Marks, illustrate the invention.

EXAMPLE I

Hydrolysed terpolymer of acrylamide, dimethyl-diallyl-ammonium chloride, and diethyl-diallyl-ammonium chloride.

5 To make 100 lbs. of a terpolymer of, by weight, 50% acrylamide, 2.5% diethyl-
diallyl-ammonium chloride (DEDAAC), and 47.5% dimethyl-diallyl-ammonium
chloride (DMDAAC), a charge was prepared comprising 74.8 lbs. water, 10 lbs. 5
acrylamide, 0.870 lbs. DEDAAC, (as 57% solution) and 14.3 lbs. DMDAAC, (as
a 66.5% solution). After the addition of small amounts of EDTA and sodium salicylate
10 (100 ppm), the pH was adjusted to 6.5, and the charge was purged with nitrogen gas
for one hour. 11.09 grams of ammonium persulfate in a small amount of water was
then added and mixed for 5 minutes. 4.89 grams of sodium bisulfite in 250 ml/H₂O 10
and a small amount of copper sulfate solution were then pumped into the reactor
at a rate between 2 and 2/5 ml/min. until consumed. The reaction completed at
15 about 75° C. Temperature was allowed to recede to 60° C where it was held for
one hour. The fully reacted polymer was then hydrolysed by pumping into it a 20%
solution of KOH at a rate of 26.5 ml/min. for 30 minutes. It was mixed for two addi- 15
tional hours at 60° C, and the resulting polymer solution was drum-dried to recover
the pure polymer. The polymer was hydrolysed to the extent of ten mole percent
of the quaternary ammonium groups.

20 The partially hydrolysed polymer produced above was used as a retention aid in
the laboratory production of a typical bond paper by making 43 lb./3000 ft.² hand
sheets using a valley handsheet machine. The retention aid was added to the wet
pulp slurry corresponding to a head box addition in an amount equivalent to 1/2
25 pound of the retention aid per ton of dry pulp. In this series of laboratory experi-
ments different levels of alum were used to determine the effect of changes in alum
loading upon retention.

The results are shown in Table I.

TABLE I

Percent retention of pigment (pH — 4.9, adjusted with H₂SO₄)

	0 lb/ton Alum	40 lb/ton Alum	80 lb/ton Alum
With retention aid of Example I	82.8	81.5	79.8
Without retention aid	48.6	54.6	55.2

30 This polymer was also compared to a cationic polymer, "Reten 205", which is
believed to be a copolymer of acrylamide (95% by weight) and the methosulfate salt
of dimethyl-amino-ethyl methacrylate, and also to "Separan PG—24", a slightly 30
anionic polymer believed to be a homopolymer of acrylamide in which 5% of the
amide groups are hydrolysed to carboxylic acid groups. The comparison was made
on the retention of TiO₂ in a system using bleached sulfite pulp beaten to a Canadian
35 Standard Freeness of 260 ml. The system contained one percent rosin, 15 percent
TiO₂ and various amounts of alum. Handsheets having basis weights of 37.5 pounds
were formed after the aid was added and the retention determined. The results are
shown in Table II.

TABLE II

Percent Retention of Fines

Polymer	Feed rate lbs/ton dry pulp	pH 6.3 10 lb/ton alum loading	pH 5.5 20 lb/ton alum loading	pH 4.8 40 lb/ton alum loading
Control	0	55.5	61.2	56.9
Ex 1	0.37	75.2	81.1	81.4
Ex 1	0.31	74.2	80.6	79.7
Ex 1	0.275	71.4	78.9	78.2
Separan PG—2	0.5	66.0	78.9	76.9
Reten 205	0.4	73.5	75.0	62.6

EXAMPLE II

Hydrolysed terpolymer of acrylamide, DMDAAC, and diallyl-beta-propionamido-methyl-ammonium chloride.

5 The system of Example I was followed to produce a polymer of 47.5% DMDAAC, 50.0% acrylamide, and 2.5% of the beta-propionamido compound. As with Example I, the polymerization reaction was completed at 75° C, the temperature was lowered to 60° C for one hour, and the polymer hydrolysed to the extent of 10% of the number of quaternary ammonium groups by pumping a 20% solution of KOH into the product for 30 minutes at 25.9 ml/min. 10

EXAMPLE III

Hydrolysed terpolymer of 50% acrylamide, 2.5% carboxymethyl-beta-propionamido-diallyl-ammonium chloride, and 47.5% DMDAAC.

15 Again, a 20% monomer batch solution was made and polymerized as in Example I. It was hydrolysed by introducing a 45% KOH solution at a rate of 11.8 ml/min. for 30 minutes. 15

EXAMPLE IV

20 The three products made in Examples I to III were field-tested in a paper mill making label paper. The basis weight on this grade was 44 lb/3000 Ft² and the furnish used was a mixture of virgin hardwood and soft wood pulp. This was a rosin-sized, filled sheet. The alum loading in the system was 30—40 lb./ton and gave a white-water pH of 4.1 to 4.4. 20

25 The fillers used were TiO₂ and clay which were fed continuously to the stock immediately prior to the head box. The three products were fed at 0.5 lb. retention aid per ton of finished paper and yielded a 37% reduction in the amount of TiO₂ needed to meet a minimum opacity specification. Tests with and without the retention aid showed no adverse effects on Mullen, tear, wax pick, or brightness. There was no discernable difference in retention between the three products. 25

EXAMPLE V

30 1%-hydrolysed terpolymer of acrylamide, DEDAAC and DMDAAC. 30
This example was identical to the preparation of Example I, except that it was hydrolysed to one-tenth the extent of Example I, e.g. by pumping a 20% KOH solution into the polymer solution at a rate of 2.6 ml/min.

EXAMPLE VI

35 The product made in Example V was field-tested in a paper mill making printing grade paper. The furnish used in the paper was 1:1 mix of bleached groundwood and bleached kraft. The filler used was clay and the system pH was 3.9—4.1 adjusted with H₂SO₄. There was little or no alum in the system. One-pass filler retention increased from 15% to 34% with the addition of 0.2 lb/ton, an increase of 56%. 35

EXAMPLE VII

50%-hydrolysed terpolymer of acrylamide, DMDAAC, and DEDAAC.

In this case, a polymer was made consisting of 70% acrylamide, 1.5% DEDAAC, and 28.5% DMDAAC following the general polymerization procedure set out above. It was hydrolysed to the extent of 50% of the quaternary ammonium by introducing to the polymer solution a 20% KOH solution at a rate of 76 ml/min. for 30 minutes. The batch was then held for 2 hours at 60° C and drum dried.

EXAMPLE VIII

The polymer produced in Example VII was used as a retention aid in the laboratory production of a typical bond paper using a valley handsheet machine to make a sheet 42 lb/3000 sq. ft. The filler used was TiO₂ at 10% based on the weight of furnish (bleached sulfite). The retention aid was added to the wet pulp slurry corresponding to a head-box addition in an amount equivalent to 1/2 pound of the retention aid per ton of dry pulp. In this series of laboratory experiments different amounts of alum were used to determine the effect of changes in alum loading upon retention. Results are shown in the following table.

TABLE III

Percent Retention of TiO₂ (pH — 4.7, adjusted with H₂SO₄)

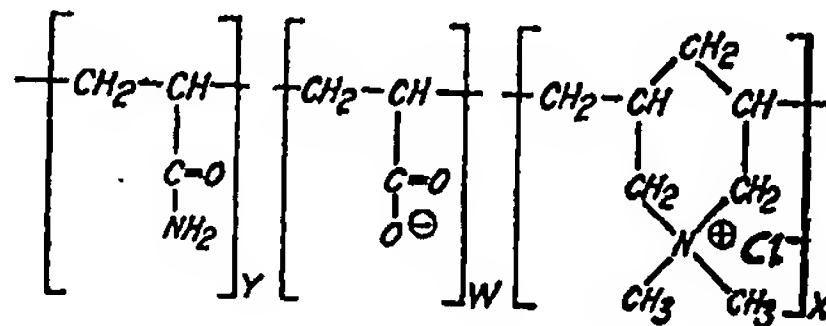
	0 lb/ton alum	20 lb/ton alum	40 lb/ton alum	80 lb/ton alum
With retention aid	62%	75%	88%	86%
Without retention aid	45%	52%	66%	63%

EXAMPLE IX

A monomer mixture of 20% total solids in aqueous solution was formed from the following monomers:

60 parts of dimethyl-diallyl-ammonium chloride
40 parts of acrylamide.

The redox polymerization catalyst system set forth in Example I was added to this monomer solution, and polymerization was effected at 59° C for about one hour. The amide groups in the resultant polymer were hydrolysed by a 20% solution of sodium hydroxide, at a temperature of about 60° C for 2½ hours. The resultant high-molecular-weight water-soluble amphoteric polymer was used as a retention aid in the production of bond paper, and exhibited good retention and drainage properties with little or no change in these properties caused by varying either pH or alum loading. The hydrolysed polymer contained units of formulae

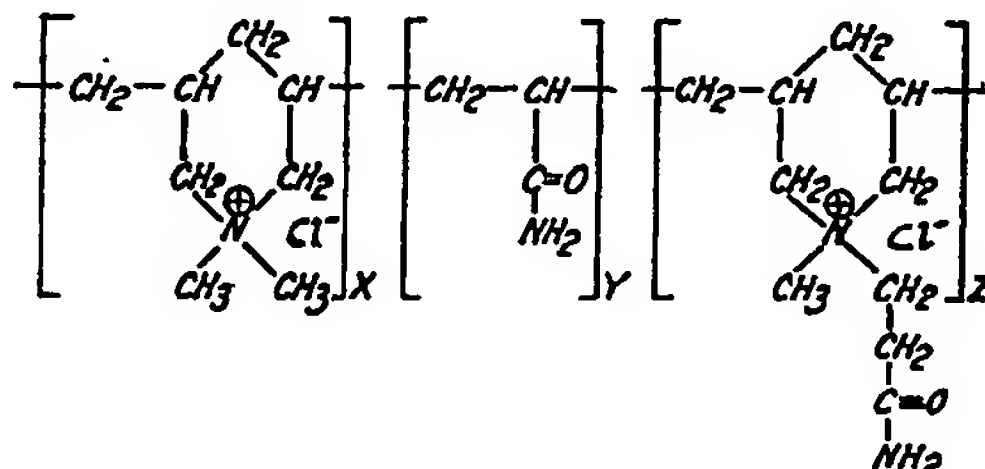


where $\frac{Y+W}{X}$ was 40/60, and X/W was 10/0.8.

EXAMPLE X

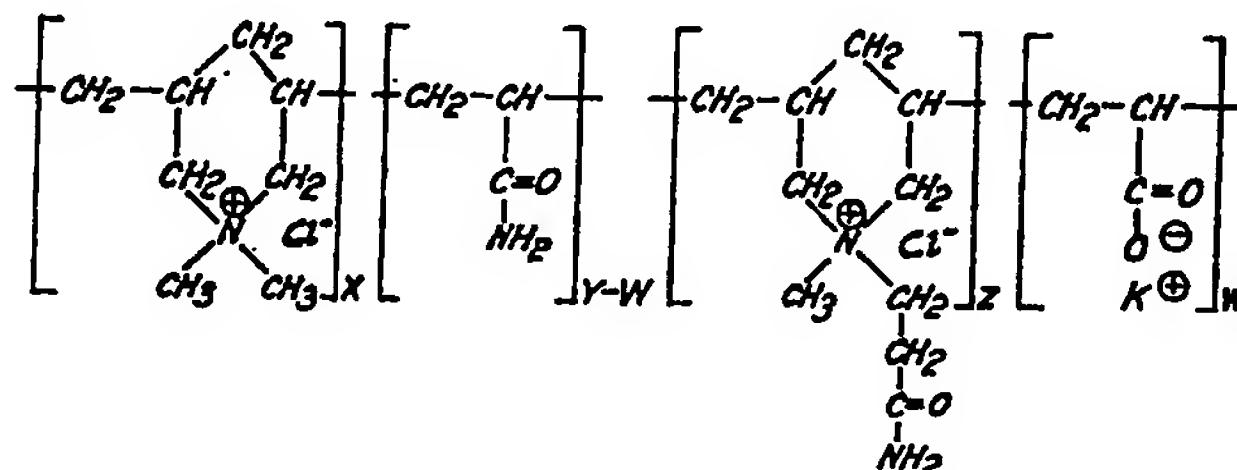
Diallyl-dimethyl-ammonium chloride (38 parts by weight), acrylamide (60 parts by weight), and diallyl-methyl-beta-propionamido-ammonium chloride (2 parts by

weight) were dissolved in an aqueous solution at a total solids concentration of 25%. To this solution a redox polymerization catalyst composed of an aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $\text{Na}_2\text{S}_2\text{O}_5$ was added and allowed to react to completion, the temperature was held at about 60° C for about an hour. An aqueous solution of a water-soluble polymer was formed contained units of formulae



where the ratio $(X+Z):Y$ was 40:60, and the ratio of $Z:X$ was 2:38.

The base polymer was hydrolysed by treating the same with an appropriate amount of a 15% solids potassium hydroxide solution at a temperature of about 60° C for about 2 hours, and the resulting hydrolysed polymer contained units of formulae

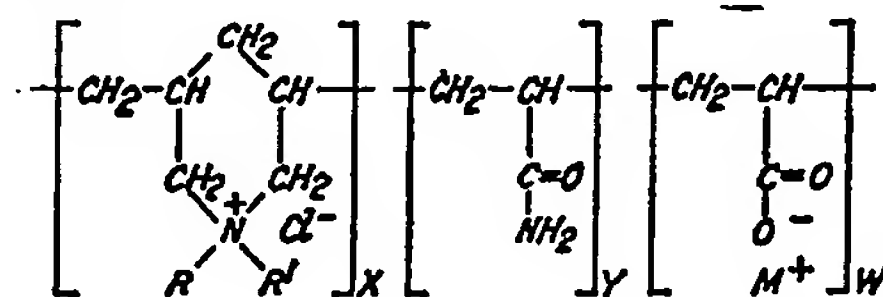


where the ratio of $X+Z/W$ was 10/1.8.

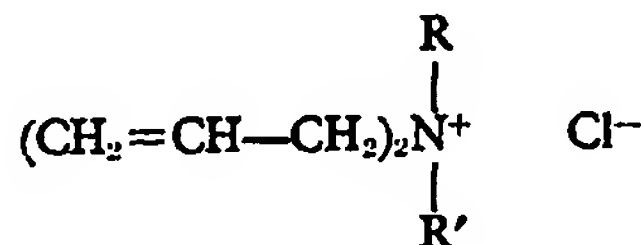
This partially hydrolysed polymer is useful as a retention aid.

WHAT WE CLAIM IS:

1. A method of improving the retention of inorganic filler and fine cellulosic material in the production of paper that comprises adding to an aqueous paper pulp suspension a linear amphionic copolymer of molecular weight at least 10000 having units of the general formulae:



in which each of R and R', which are similar or dissimilar, is a C_{1-18} alkyl, β -pionamide or carboxymethyl radical and w, x and y are such that $(w+y):x$ lies within the range obtained by copolymerizing acrylamide and a diallyl-quaternary-ammonium chloride of formula:



in a weight ratio of from 3:7 to 7:3, $x:w$ is from 100:1 to 2:1 and M^+ is an alkali-metal or ammonium cation.

2. A method as claimed in claim 1 in which the diallyl-quaternary-ammonium chloride is a mixture of substantially 95% by weight dimethyl-diallyl-ammonium chloride and substantially 5% by weight diethyl-diallyl-ammonium chloride, the ratio of acrylamide to the said mixture is about 1:1, and $x:w$ is about 10:1.

3. A method as claimed in claim 1 or 2 in which the copolymer is added at a rate of about 0.1 to 5 pounds copolymer per ton of dry pulp.

4. A method as claimed in claim 1 or 2 in which about 0.1 pound of the copolymer is added per ton of dry pulp.

5 5. A method as claimed in any one of claims 1—4 in which the copolymer is added to the aqueous paper pulp suspension before it is deposited on a forming surface to form a continuous aqueous paper sheet. 5

6. A method as claimed in claim 1, substantially as described in any one of Examples I, IV, VI and VIII.

10 7. A method as claimed in claim 1, in which the polymer is obtained by a process substantially as described in any one of Examples I, II, III, V, VII, IX and X. 10

8. Paper whose preparation comprises a method as claimed in any one of the preceding claims.

For the Applicants,
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